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A novel hydrophilic–hydrophobic magnetic interpenetrating polymer networks (IPNs) and its adsorption towards salicylic acid from aqueous solution

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HIGHLIGHTS

- A strategy to synthesize a novel magnetic PMADETA/PDVB IPNs was proposed.
- PMADETA/PDVB IPNs is both hydrophilic and hydrophobic.
- PMADETA/PDVB IPNs has a large equilibrium adsorption capacity to salicylic acid.
- PMADETA/PDVB IPNs has a large dynamic adsorption capacity to salicylic acid.
- PMADETA/PDVB IPNs can be regenerated and repeatedly used.

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ABSTRACT

We developed an effective strategy to synthesize a novel hydrophilic–hydrophobic magnetic interpenetrating polymer networks (IPNs) for adsorptive removal of salicylic acid from aqueous solution. The proposed magnetic poly (methyl acryloyl diethylenetriamine)/polydivinylbenzene (PMADETA/PDVB) IPNs was synthesized by interpenetration of polydivinylbenzene (PDVB) networks in the pores of the magnetic poly (glycidyl methacrylate) (PGMA) networks, and then the first PGMA networks were transformed to poly (methyl acryloyl diethylenetriamine) (PMADETA) networks by an amination reaction. The magnetic PMADETA/PDVB IPNs contained hydrophilic PMADETA networks as well as hydrophobic PDVB networks, inducing a much enhanced adsorption towards salicylic acid (228.9 mg/g at an equilibrium concentration of 100 mg/L), which was 20.8 times relative to PGMA and 12.7 times relative to PGMA/PDVB IPNs. At an initial concentration of 1037.9 mg/L and a flow rate of 1.3 mL/min, the dynamic saturated adsorption capacity was measured to be 297.0 mg/g.

1. Introduction

Salicylic acid is frequently applied as a pharmaceutical intermediate for production of medicines such as aspirin, lopirin, fenamifuril, diflunisal and benorylatum [1,2]. On the other hand, salicylic acid is a typical pollutant in the industrial wastewater and it is capable of causing serious environmental problems. It can induce headache and nausea, even affects the normal functions of the liver and kidney. Hence efficient removal and recycling of salicylic acid from wastewater is a pressing problem and has attracted increasing attentions in recent years [3–5].

Many methods and techniques including advanced oxidation process (AOP) [6], electrocoagulation [7,8], electrochemical membrane process (EMP) [9], molecular imprinting technique (MIP) [10] and adsorption [2,3] are developed for efficient removal and recycling of salicylic acid. AOP is an environmentally friendly technology for treatment of low concentration of toxic organics [11], while it is high cost because of using ozone as the oxidant and ultraviolet light as the light source [12]. Electrocoagulation is a promising technique for treatment of salicylic acid because of its versatility and environmental suitability, but additional equipment to generate the electron is needed, which increases its handling expense [7]. EMP shows high current efficiency and low energy consumption and can be employed for the separation of salicylic acid from sodium salicylate on a small scale [9]. MIP has potential application in the enrichment, separation and detection of salicylic

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acid in biological fluids [13]. Among which, adsorption is proved to be the most attractive and effective technique for removal and recycling salicylic acid from aqueous solution [2–4].

Interpenetrating polymer networks (IPNs) technology is an outstanding method for stable integration of two polymer networks with different properties or functions by physical entanglements [3,14]. During the past two decades, IPNs is found to be one of the most efficient polymeric materials in reinforced rubbers, toughened plastics, coatings and damping materials [14,15]. In particular, IPNs is one of the most efficient adsorbents for adsorptive removal of pollutants from aqueous solution because of its large equilibrium adsorption capacity, high adsorption selectivity, diverse chemical structure and easy regeneration property [16–19]. Due to the strong phase separation liability between the hydrophobic and hydrophilic networks, at present the hydrophobicity or the hydrophilicity of the two networks composed of the IPNs is very similar [20–22], and it is a great challenge to prepare the IPNs containing both of hydrophobic and hydrophilic networks. Moreover, these typical IPNs hold relatively small equilibrium adsorption capacity towards aromatic compounds with both of hydrophobic and hydrophilic portions [23]. We propose that the phase separation liability will not be serious as transforming one of the hydrophobic networks in the hydrophobic–hydrophobic IPNs to hydrophilic networks by a specific chemical reaction, and hence the hydrophilic–hydrophobic IPNs can be synthesized in a simple way [23,24]. What's more, this kind of hydrophilic–hydrophobic IPNs may have a much enhanced adsorption affinity to the aromatic compounds with both of hydrophobic and hydrophilic portions. To the best of our knowledge, few studies reported the hydrophobic–hydrophilic IPNs or hydrophilic–hydrophobic IPNs [23–27,19]. Our group [23–25] prepared a series of hydrophobic and hydrophilic IPNs, and used them to remove salicylic acid and *o*-aminobenzoic acid. Tian et al. [26] reported a hydrophobic/hydrophilic interpenetrating network composite nanofiber for the support layer of forward osmosis membrane. Liao et al. [19] synthesized a hydrophobic/hydrophilic polystyrene/polyamide interpenetrating polymer network and employed it as a polymeric adsorbent to adsorb quercetin [19].

In recent years, magnetic ion-exchange resins (MIEX) have been increasingly applied for removal of aromatic compounds from wastewater [28–32]. With the aid of magnetic field, MIEX can be easily separated from aqueous solution, and hence they are extensively employed in a complete mixed contactor process for wastewater treatment [33]. As compared with the fixed beds, the magnetic separation process can significantly increase the sewage treatment amount and reduce the operating costs. At present, most of the magnetic resins are focused on surface modification of various ion-exchange functional groups [34–37], while few studies are reported on preparation of the magnetic polymeric adsorbents with hydrophilic–hydrophobic networks.

In this study, we developed an effective strategy to greatly improve the equilibrium adsorption capacity of salicylic acid. For this purpose, hydrophobic magnetic poly (glycidyl methacrylate) (PGMA) was firstly prepared by suspension copolymerization of glycidyl methacrylate (GMA) and divinylbenzene (DVB) with the addition of oleic acid-coated Fe_3O_4 nanoparticles, then hydrophobic polydivinylbenzene (PDVB) networks were interpenetrated in the pores of the magnetic PGMA networks, and the hydrophobic–hydrophobic magnetic PGMA/PDVB IPNs was synthesized according to a typical IPNs technology. After that, an amination reaction was performed for the magnetic PGMA/PDVB IPNs and the first hydrophobic PGMA networks in the IPNs were transformed to hydrophilic poly (methyl acryloyl diethylenetriamine) (PMADETA) networks, and hence a magnetic PMADETA/PDVB IPNs was synthesized. After characterizing the magnetic PMADETA/PDVB IPNs by Fourier transform infrared spectroscopy (FT-IR), N_2 adsorption isotherms, vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM), the adsorption property of the magnetic PMADETA/PDVB IPNs was evaluated from aqueous solution by using salicylic acid as the model adsorbate, the equilibrium adsorption and column adsorption were investigated in detail.

2. Materials and method

2.1. Materials

Oleic acid (OA), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and ammonium hydroxide were purchased from Shanghai Chemical Reagents Company, China. The monomer GMA and the crosslinking reagent DVB were purchased from Gray West Chengdu Chemical Co. Ltd., and they were washed by using 5 wt% NaOH (w/v) for three times to remove the inhibitors and then dried by anhydrous magnesium sulfate. Benzoyl peroxide (BPO) was purified by recrystallization before use. Diethylenetriamine (DETA), toluene, *n*-heptane and salicylic acid were analytical reagents and used without further purification.

2.2. Preparation of the magnetic PMADETA/PDVB IPNs

As shown in Scheme 1, the magnetic PMADETA/PDVB IPNs was prepared by three continuous processes named suspension copolymerization, interpenetration and amination. OA-coated Fe_3O_4 nanoparticles were prepared by co-precipitation method [38] and dispersed in GMA (16.0 g) and DVB (4.0 g). GMA and DVB were copolymerized under N_2 protection at 348 K for 12 h with the help of the initiator BPO (0.20 g), in which toluene (22.0 g) and *n*-heptane (8.0 g) were applied as the porogens, and hence the magnetic PGMA was prepared. According to a typical interpenetration method performed in Ref. [3], 20 g of PGMA beads were firstly swollen by a mixture of DVB, toluene, *n*-heptane and BPO for 12 h, and the mass ratio of DVB to PGMA was 1:1. Toluene and *n*-heptane were employed as the porogens and they were 200% relative to DVB and the mass ratio of toluene to *n*-heptane was pre-set to be 4:1. The swollen magnetic PGMA beads were filtered from the mixture and added into 200 mL 0.05% of polyvinyl alcohol aqueous solution (w/v). At a moderate stirring speed, the temperature of the reaction mixture was raised to 368 K and the reaction mixture was kept at this temperature for 12 h. Thereafter, the obtained hydrophobic–hydrophobic magnetic PGMA/PDVB IPNs were chemically transformed to hydrophilic–hydrophobic magnetic PMADETA/PDVB IPNs via an amination reaction with superfluous DETA at 393 K for 12 h.

2.3. Characterization of the magnetic PMADETA/PDVB IPNs

FT-IR spectra of the IPNs were recorded on a Nicolet 510P Fourier transform infrared instrument in 500–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. The BET surface area, pore volume, and pore diameter distribution of the IPNs were determined by N_2 adsorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The morphology of the IPNs was observed using transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The magnetization curves of the IPNs were measured by a vibrating sample magnetometer (VSM, Lakeshore 7307) at 300 K.

2.4. Adsorption isotherms

About 0.1000 g of the IPNs was mixed with a series of salicylic acid aqueous solutions with the initial concentration of 196.8,